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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **POLYMERISATION INHIBITOR**

(57) Abstract: A polymerisation inhibitor comprising a non-hindered cyclic hydroxylamine either alone or in combination with an additional inhibitor.

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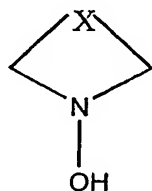
POLYMERISATION INHIBITOR

This invention relates to compositions for inhibiting polymerisation of unsaturated monomers, particularly vinyl, α -olefin, acrylic, conjugated diene or other ethylenically unsaturated monomers, and most particularly vinyl aromatic compounds, especially styrene. This invention also relates to a method of inhibiting polymerisation of such monomers.

US 2965685 discloses use of N, N-dialkylhydroxylamines to prevent polymerisation of styrene. Various combinations of N, N-dialkylhydroxylamines with other inhibitors have been disclosed.

According to a first aspect of the present invention there is provided a polymerisation inhibitor comprising a non-hindered cyclic hydroxylamine either alone or in combination with an additional inhibitor.

The non-hindered cyclic hydroxylamine is a cyclic hydroxylamine having no alkyl or other alpha substituents adjacent the hydroxylamine group. Preferred compounds have the formula (1).



(1)

wherein X is a group selected from: $(CH_2)_m Y (CH_2)_n$ wherein m and n are each independently an integer from 0 to 5 and Y is a CH_2 , or a hetero atom eg O, S or NH and wherein one or more CH_2 is optionally substituted with one or more C_1 - C_5 alkyl groups; $-(CH_2)_r - CH = CH - (CH_2)_s -$ wherein r and s are independently integers from 0 to 3, optionally substituted with one or more C_1 - C_5 alkyl groups.

Preferred examples include: 1-hydroxypiperidine, 4-hydroxymorpholine, 1-hydroxypyrrolidine, 1-hydroxyazetidine, 1-hydroxy-2,5-dihydropyrrole, 1-hydroxyhexamethyleneimine, 1-hydroxyazocan. Partially saturated aromatic bi or tricyclic unhindered hydroxylamines may also be employed, for example, selected from:
5 1-hydroxy-2,3,4-trihydroquinoline, 9-hydroxycarbozole and 1-hydroxy-2,3-dihydroindole. These compounds may be optionally substituted with one or more C₁-C₅ alkyl groups.

Mixtures of compounds may be employed.

Particularly preferred compounds are selected from: 1-hydroxypiperidine, 4-hydroxymorpholine and mixtures thereof.

10 The inhibitor in accordance with the first aspect of this invention may be used in combination with one or more co-inhibitors eg nitrophenols such as 2,4-dinitrophenol (DNP) or substituted nitro phenols such as 2-*sec*-butyl-4,6-dinitrophenol (DNBP). Alternative co-inhibitors may be selected from free radicals (SFR's) such as 4-hydroxy TEMPO, 4-oxo TEMPO, and 4-amino TEMPO, t-alkylcatechols, t-alkylhydroquinones,
15 benzoquinones, p-phenylene diamines and other inhibitors known to those skilled in the art.

The amount of co-inhibitor may be in the range from a trace (eg 1%) to 96%, preferably 40 to 96% by weight of the total amount of inhibitor.

Percentages and other proportions referred to in the specification are by weight
20 unless indicated otherwise. Percentages and proportions may be selected from ranges referred to in the specification to total 100%.

According to a second aspect of the present invention a polymerisation inhibited composition comprises a monomer and an inhibitor in accordance with the first aspect of this invention.

According to a third aspect of this invention a method of inhibiting polymerisation during production, purification, storage or use of a vinyl, α -olefin, acrylic, conjugated diene or other ethylenically unsaturated monomer comprises the step of addition to the monomer of a polymerisation inhibitor in accordance with the first aspect of the present invention.

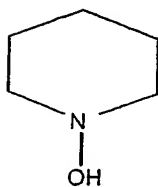
Unhindered cyclic hydroxylamines in accordance with the present invention have been found to be excellent polymerisation inhibitors, particularly of vinyl aromatic compounds, especially at elevated temperatures. 1-hydroxypiperidine and 4-hydroxymorpholine have been found to be particularly effective inhibitors of styrene polymer formation, both on their own and in combination with 2-*sec*-butyl-4,6-dinitrophenol (DNBP). Unfavourable premature polymerisation in processing steps such as the production, purification, storage, shipment preparation and use of these monomers or in a mixture of the monomers or a hydrocarbon mixture containing such monomers. Premature polymerisation can cause contamination of the monomer and degradation of the properties of the monomer. A polymer can be deposited in the apparatus. Formation of popcorn polymer is particularly undesirable. The polymerisation inhibitor in accordance with the first aspect of the present invention is effective not only for monomers and mixtures thereof but also for hydrocarbon mixtures and the like containing a small proportion of the monomers.

The invention is further described by means of examples but not in any limitative sense.

Unhindered cyclic hydroxylamines are disclosed in US 2843481 (Polaroid) and may be prepared by oxidation of the corresponding amines with aqueous hydrogen peroxide at less than 20°C.

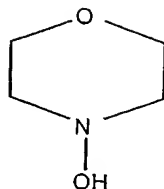
Structures:

-4-



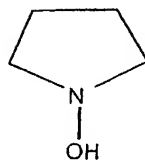
1-H P

M w = 101



4-H M

M w = 103

1-hydroxy-
pyrrolidine

M w = 87

Results

(a) Efficacy

5 Evaluation of the efficacy of hydroxylamines was carried out using a continuous stirred tank reactor (CSTR). These mimic the reboiler of a styrene distillation column. The styrene has a residence time of approximately two hours inside the reactor.

Two CSTRs were used to gather this data. For any given temperature the same CSTR was used for all experiments at that temperature.

10 120°C CSTR – dead volume was 170 ml. With a styrene flow rate of 75ml/hr the steady state was reached in 4.5 hrs (2 flask volumes). Data gathered after this temperature was averaged to give the steady state polymer level.

110° and 100°C CSTR – dead volume was 150 ml. With a styrene flow rate of 75 ml/hr the steady state was reached in 4 hrs. Data gathered after this point were averaged to give the steady state polymer level.

15 Nitrogen sparging to remove oxygen was at a measured rate of 200 ml/minute in all experiments. Aside from the inhibitors under test the only variable was the inherent variation in the rate of thermal initiation of styrene polymerisation.

20 Hydroxylamines were tested on their own and in combination with DNBP as shown in Table 1 (below). By way of comparison results are also presented for prior art styrene inhibitor mixtures, namely 4-Hydroxy tempo with DNBP, 4-Oxo tempo with DNBP and dihydroxypropylhydroxylamine (DHPHA) with DNBP. At a test temperature of 120°C the results shown in Table 1 were obtained (polymer results to nearest 50 ppm).

Results within 10% of each other have been ranked as equal.

Table 1 - Results at 120°C Total inhibitor is 400 ppm

Component 1	Wt %	Component 2	Wt %	Average Polymer at Steady State (ppm)	Rank
1-HP	100			1850	1
DNBP	90	1-HP	10	2500	2=
DNBP	90	4-HM (100%)	10	2600	2=
DNBP	95.5	4-Oxo Tempo	4.5	2350	2=
DNBP	90	4-Hydroxy Tempo	10	3200	5=
DNBP	100			3350	5=
DNBP	90	DHPHA	10	3450	5=
4-HM (100%)	100			Failed in 3.5 hours	9

Batch tests were also carried out. This was to determine the optimum ratio of DNBP and 4-HM. This was found to be about 7 parts DNBP to about 3 parts 4-HM.

A further continuous test was carried out using this ratio;

Table 1a

Component 1	Wt %	Component 2	Wt %	Average Polymer at Steady State (ppm)	
DNBP	70	4-HM (100%)	30	1200	

A further test employed a mixture of 1-Hydroxypiperidine and 4-Hydroxy Tempo. This mixture showed synergy, the results are shown in Table 1b.

Table 1b

Component 1	Wt %	Component 2	Wt %	Average Polymer at Steady State (ppm)
1-HP	100			1850
1-HP	90	4-HT	10	450

- 5 At 110°C the results shown in Table 2 were obtained. 4-HM technical grade (65%) showed excellent performance as a single inhibitor at this temperature and therefore the 100% active ingredient was not tested.

Table 2 - Results at 110°C Total inhibitor is 250 ppm

Component 1	Wt %	Component 2	Wt %	Average Polymer at Steady State (ppm)	Rank
1-HP	100			100	1
DNBP	90	4-HM (100%)	10	250	2
4-HM (65%)	100			700	3=
DNBP	90	1-HP	10	1100	5
DNBP	90	4-Hydroxy Tempo	10	1600	6
DNBP	90	DHPHA	10	1900	7
DNBP	95.5	4-Oxo Tempo	4.5	2400	9=
DNBP	100			2400	9=

At 100°C the results shown in Table 3 were obtained. As before, the results were given to the nearest 50 ppm of polymer and results within 10% of each other were classes as equivalent.

Table 3 - Results at 100°C Total 100 ppm inhibitor

Component 1	Wt %	Component 2	Wt %	Average Polymer at Steady State (ppm)	Rank
1-HP	100			250	1
DNBP	90	4-HM (100%)	10	450	2
DNBP	90	4-Hydroxy Tempo	10	750	3
4-HM (65%)	100			1000	4
DNBP	90	DHPHA	10	1900	56
DNBP	95.5	4-Oxo Tempo	4.5	2150	67=
DNBP	90	1-HP	10	2300	67=
DNBP	100			2750	89
DNBP	100			2400	9=

4-Hydroxymorpholine in 3 component systems

In this test N-bis-(1,4-dimethylpentyl)-p-phenylenediamine (PD) was used as a third component. The results are shown in Table 4.

Table 4 - Three component mixtures

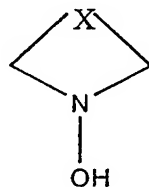
Test Mixture	Polymer formed at 120°C (ppm)	Polymer formed at 100°C (ppm)
DNB/PD/DHPHA	2750	250
DNBP/PD/4-HM	1350	100

4-Hydroxymorpholine is clearly a superior enhancer of the DNB/PD system than is DHPHA under our test conditions. It was noted that at 120°C this three component system is equivalent in performance to the two component DNB/P4-HM system.

CLAIMS

1. A polymerisation inhibitor comprising a non-hindered cyclic hydroxylamine either alone or in combination with an additional inhibitor.

2. A polymerisation inhibitor as claimed in claim 1, wherein the non-hindered cyclic hydroxylamine is cyclic hydroxylamine having no alkyl or other alpha substituents adjacent the hydroxylamine group. Preferred compounds have the formula (1).



(1)

wherein X is a group selected from: $(CH_2)_m Y (CH_2)_n$ wherein m and n are each independently an integer from 0 to 5 and Y is a CH_2 , or a hetero atom eg O, S or NH and wherein one or more CH_2 is optionally substituted with one or more C_1 - C_3 alkyl groups; $-(CH_2)_r - CH = CH - (CH_2)_s -$ wherein r and s are independently integers from 0 to 3, optionally substituted with one or more C_1 - C_3 alkyl groups.

3. A polymerisation inhibitor as claimed in claim 2, wherein the hydroxylamine is selected from the group consisting of: 1-hydroxypiperidine, 4-hydroxymorpholine, 1-hydroxypyrrolidine, 1-hydroxyazetidine, 1-hydroxy-2,5-dihydropyrrole, 1-hydroxyhexamethyleneimine, 1-hydroxyazocan.

4. A polymerisation inhibitor as claimed in claim 2, wherein the hydroxylamine is selected from the group consisting of partially saturated aromatic bi or tricyclic unhindered hydroxylamines and mixtures thereof.

5. A polymerisation inhibitor as claimed in claim 4, wherein the hydroxylamine is selected from the group consisting of: 1-hydroxy-2,3,4-trihydroquinoline, 9-hydroxycarbozole and 1-hydroxy-2,3-dihydroindole, optionally substituted with one or more C₁ – C₅ alkyl groups, and mixtures thereof.

5 6. A polymerisation inhibitor as claimed in claim 3, wherein the hydroxylamine is selected from the group consisting of: 1-hydroxypiperidine, 4-hydroxymorpholine and mixtures thereof.

7. A polymerisation inhibitor as claimed in any preceding claim, wherein the co-inhibitor is selected from the group consisting of nitrophenols, substituted nitrophenols and stable free-radicals.

8. A polymerisation inhibitor as claimed in claim 7, wherein the inhibitor is selected from: 2,4-dinitrophenol, 2-sec-butyl-4,6-dinitrophenyl, 4-hydroxy tempo, 4-oxo tempo, 4-amino tempo, t-alkylcatechols, t-alkylhydroxyquinones, benzoquinones, and p-phenylene diamines.

9. A polymerisation inhibitor as claimed in claim 7 or 8, wherein the amount of co-inhibitor is in the range from a trace to 96% by weight of the total amount of inhibitor.

10. A polymerisation inhibitor as claimed in claim 9, wherein the amount of co-inhibitor is 40 to 96% by weight of the total amount of inhibitor.

11. A polymerisation inhibited composition comprising a monomer and an inhibitor as claimed in any preceding claim.

12. A method of inhibiting polymerisation during production, purification, storage or use of a vinyl α -olefin, acrylic, conjugated diene or other ethylenically unsaturated monomer comprising the step of addition to the monomer of a polymerisation inhibitor as claimed in any of claims 1 to 10.

INTERNATIONAL SEARCH REPORT

PCT/GB 03/02367

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C7/20 C07C239/08 C07C239/12 C07C239/16 C07D205/04
 C07D207/04 C07D207/20 C07D209/04 C07D209/86 C07D225/02
 C07D295/02 C07D295/22 C07D215/06 C07D211/94 C08K5/3435

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C07D C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 265 751 A (GEORGE MCCOY ET AL) 9 August 1966 (1966-08-09)	1-3,6, 11,12
Y	the whole document	4,5,7-10
X	US 3 265 752 A (CASE WHITON ALFRED ET AL) 9 August 1966 (1966-08-09)	1-3,6, 11,12
Y	the whole document	4,5,7-10
X	WO 00 14175 A (A H MARKS AND COMPANY LIMITED ; BUSHBY RICHARD (GB); LORD NIGEL (GB) 16 March 2000 (2000-03-16)	1-3,6-12
Y	*abstract, page 3, lines 6-26; page 4, last paragraph; page 5, first paragraph and claims 1-5*	4,5

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

26 August 2003

Date of mailing of the international search report

08/10/2003

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

PCT/GB 03/02367

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; retrieved from CA Database accession no. 1998:643472 XP002252353	1-3,11, 12
Y	abstract & LI, ZHANG, JIA AND HU: "Inhibition effect on radical polymerization of vinyl monomers.XXI. Studies on behavior of some substituted hydroxylamine in the copolymerization of styrene with methyl methacrylate" LANZHOU DAXUE XUEBAO, ZIRAN KEXUEBAN, vol. 34, no. 1, 1998, pages 69-75,	4-10
X	DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; retrieved from CA Database accession no. 1993:255417 XP002252354 abstract & ZHANG, LI AND YANG: "Inhibiting effect of radical polymerization of vinyl monomers.(XV). Behavior of some substituted hydroxylamines in the copolymerization of styrene with acrylonitrile" GAODENG XUEXIAO HUAXUE XUEBAO, vol. 13, no. 10, 1992, pages 1319-1322,	1-3,11, 12
X	DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; retrieved from CA Database accession no. 1991:164864 XP002252355	1-3,11, 12
Y	abstract & ZHANG, LI, BAI AND LU: "Inhibiting effect of radical polymerization for vinyl monomers. XI. Studies on the inhibition and their chain transfer constants of substituted hydroxylamine compounds in bulk polymerization of vinyl acetate and acrylonitrile" GAOFENZI XUEBAO, vol. 2, 1990, pages 239-243,	4-10

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INTERNATIONAL SEARCH REPORT

PCT/GB 03/02367

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; retrieved from CA Database accession no. 1991:164863 XP002252356	1-3, 11, 12
Y	abstract & ZHANG, LI, WANG, LU AND FENG: "Inhibiting effects of radical polymerization of vinyl monomers. X. Studies on the inhibition and its mechanism of hydroxylamines compounds in free radical polymerization of styrene" GAOFENZI XUEBAO, vol. 2, 1990, pages 233-238, ---	4-10
X	DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; retrieved from CA Database accession no. 1990:217575 XP002252357	1-3, 11, 12
Y	abstract & WANG, FENG, CAI, ZHANG, LU AND LI: "An ESR study of nitroxide radicals produced in the radical polymerization of vinyl monomers" BOPUXUE ZAZHI, vol. 6, no. 3, 1989, pages 369-376, ---	4-10
X	DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; retrieved from CA Database accession no. 1986:627842 XP002252358 abstract & BORTOLUS, DELLONTE, FAUCITANO AND GRATANI: "Photostabilizing mechanisms of hindered-amines light stabilizers: interaction with electronically excited aliphatic carbonyls" MACROMOLECULES, vol. 19, no. 12, 1986, pages 2916-2922, ---	1-3, 11, 12
X	US 2 843 481 A (BLOUT ELKAN R ET AL) 15 July 1958 (1958-07-15) the whole document ---	1-3, 6
X	US 6 031 130 A (MOTOKI MASUJI ET AL) 29 February 2000 (2000-02-29)	1-4, 6
Y	*abstract; column 1, lines 1-24; column 4, lines 7-67; column 5 and example 5* ---	5, 7-12
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INTERNATIONAL SEARCH REPORT

PCT/GB 03/02367

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; retrieved from BEILSTEIN Database accession no. 1129 XP002252345 abstract & WOLFFENSTEIN: CHEM. BER., vol. 28, 1895, page 1465</p>	1,2
X	<p>DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; retrieved from BEILSTEIN Database accession no. 12432 XP002252346 abstract & MOEHRLE, H. AND LAPPENBERG, M.: ARCH. PHARM., no. 311, 1978, pages 692-697,</p>	1,2,4
X	<p>DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; retrieved from BEILSTEIN Database accession no. 1560342 XP002252347 abstract & KREHER AND PAWELCZYK: TETRAHEDRON LETT., 1966, pages 2591-2594,</p>	1-3
X	<p>DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; retrieved from BEILSTEIN Database accession no. 1421020 XP002252348 abstract & MURAHASHI, MITSUI, WATANABE AND ZENKI: TETRAHEDRON LETT., vol. 24, no. 10, 1983, pages 1049-1052,</p>	1-3
Y	<p>EP 0 512 951 A (CIBA GEIGY AG) 11 November 1992 (1992-11-11) *abstract; pages 2 and 3; page 6, lines 6-56; examples 4, 6, 9-13 and the claims*</p>	1-12

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INTERNATIONAL SEARCH REPORT

PCT/GB 03/02367

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 446 220 A (ARHANCET GRACIELA B) 29 August 1995 (1995-08-29) *abstract; column 2, lines 25-68; column 3, first paragraph; the examples and the claims* -----	1-12

INTERNATIONAL SEARCH REPORT

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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims 1-11 are product claims. Therefore any cyclic hydroxylamine which fulfils the requirements disclosed in the claims/composition including them is novelty destroying for the subject-matter of the claims.

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty for claims 1-4 and 6-11. So many documents were retrieved that it is impossible to determine which parts of the claims may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claims is impossible. Only some of the documents found are mentioned in the search report.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

PCT/GB 03/02367

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3265751	A	09-08-1966	NONE	
US 3265752	A	09-08-1966	NONE	
WO 0014175	A	16-03-2000	AU 5752299 A WO 0014175 A1	27-03-2000 16-03-2000
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